S-99/37

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICANT: PIERRE DOURNEL :

SERIAL NO: 10/070,979 : ART UNIT: 1732

FILED: September 5, 2000 : EXAMINER: KUHNS, A.R..

FOR: : PROCESS FOR THE MANUFACTURE OF POLYMERIC FOAMS

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.... :

Asst. Commissioner for Patents
Washington, D.C. 20231

I HEREBY CERTIFY THAT THIS CORRESPONDENCE IS BEING DEPOSITED WITH THE UNITED STATES POSTAL SERVICE AS FIRST-CLASS MAIL IN AN ENVELOPE ADDRESSED TO: ASST. COMMISSIONER FOR PATENTS, WASHINGTON D.C. 20231 ON THIS _______ DAY OF ________________ 2001. BY:

RULE 131 DECLARATION OF PIERRE DOURNEL

I, Pierre Dournel, am a citizen of France, hereby declare and say as follows:

1. In view of my qualifications outlined in my attached c.v., I consider myself to be an expert and to be skilled in the art of the hydrofluorocarbons and blowing agents.

2. I am the sole inventor of the above identified application.

3. Before November 12, 1998, I conceived a blowing agent mixture comprising 1,1-difluoroethane, 1,1,1,2-tetrafluoroethane and ethanol.

4. Before November 12, 1998, I had a test performed which reduced to practice the invention, wherein a blowing agent mixture comprising 1,1-difluoroethane, 1,1,1,2-tetrafluoroethane and ethanol in weight proportions (1,1-difluoroethane/1,1,1,2-tetrafluoroethane/ethanol) (70/30/5) was used to manufacture a closed cell extruded polystyrene foam board. Said test is described in the appended note.

5. The resulting foam had a closed cell content of more than 96% and showed good long –term insulating properties.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issues thereon.

Pierre Dournel

Date: october 11th, 2004

From : P.Dournel RU101 PID/MDS

[redacted]

Distribution :

1 ex. FJN for DOC RU101 (E9 5877)
1 ex. SFD-M (W.Moritz, P.Roumegoux)
1 ex. SFD-AS (P.Barthélemy → L.Zipfel)
1 ex. H.Kersten (DNF-UOF)
1 ex. PID

COMPANY : BUBBLE & FOAM INDUSTRIES (Anzegem - B)

DATE : [redacted]

VISITED BY : P.Dournel (RU101)
A.Schrouben (RU101)
H.Kersten (UOF)

RECEIVED BY : M. Vanderbauwhede
J.Naessens

SUMMARY

A new trial has been performed at BUBBLE&FOAM with a blend HFC-134a / HFC-152a / EtOH. Based on the results of the previous trial, we decided to increase the amount of HFC-152a in the blend in order to get closer to the required density.
The selected composition was 30 parts HFC-134a , 70 parts HFC-152a and 5 parts of Ethanol.
Besides, the temperatures of the process have been controlled in depth in order to avoid the formation of open cells.
During this trial, panels with a density close to 39 kg / m^3 and with various thicknesses (from 4 to 7 cm) could be produced without any surface defects.
We could also determine the solubility limit of the blend used. This solubility is between 8.5 and 9 % rated to the PS while the theoretical value for a density of 35 kg / m^3 would be 9.5 %.

1. INTRODUCTION

A new XPS trial has been performed at BUBBLE&FOAM with a blend HFC-134a / HFC-152a / EtOH.

The composition has been modified based on the results of the previous trial performed with a 50 / 50 blend and with 5 % of ethanol. In order to get closer to the required density (35 kg / m^3), the amount of HFC-152a has been increased.
The selected composition was HFC-134a / HFC-152a / EtOH (30 / 70 / 5).

2. SUMMARY OF THE PREVIOUS TRIAL

During the previous trial, it has been possible to produce XPS panels with a density between 42 and 45 kg / m^3 (measured with the skin). The surface of the panels presented however some defects strips and holes could be found inside the foam. This has been attributed to solubility limit of the 50 / 50 blend (HFC-134a / HFC-152a).
The evaluation of the basic properties of the foam showed that the thermal conductivity was initially very high (30 mW / m.K) with an increase up to 35 mW / m.K after two weeks ageing. This has been explained by the content of open cells (close to 60 %).

3. DESCRIPTION OF THE TRIAL

3.1. INITIAL CONDITIONS

As usual, the line has been started with the blend HCFC-22 / HCFC-142b.
The initial conditions of extrusion are listed in table 1.

PS flow rate (kg / h)	Gas flow rate (kg / h)	Blowing agent (%)	Temperature Extruder 1	Temperature of melt (before die)	Pression (bar)
700	84	12	190	125	180

No particular problem has been noticed during starting of the line .
The panels were produced with a density of 34 kg / m^3 and a thickness of 5 cm.

After stabilization, the blowing agent has been changed and the parameter of the extrusion has been changed as explained in table 2.

PS flow rate (kg / h)	Gas flow rate (kg / h)	Blowing agent (%)	Temperature Extruder 1	Temperature of melt (before die)	Pression (bar)
700	56	8	170	125	220

Comments :

- The gas flow rate has been reduced because of the higher blowing efficiency of the blend HFC-134a / HFC-152a. Indeed, due to the difference in molecular weight, 80 % of the quantity used is necessary. It means that the ratio of blowing agent rated to the PS has to be 9.5 % (79 % of 12) to obtain the same density. Because of the low solubility of the blend, we chose to start with a lower ratio in order to stabilize the line and then to increase it stepwise up to 9.5 %.
- The temperature in the melting extruder has been reduced in order to make cooling easier and to reduce the melt temperature before the die. This parameter is important both for the surface aspect and for the open cells content.
- The pressure of the extruder has been increased in order to increase the solubility of the gas in the melt.

The temperature of the melt before the die can not be monitored easily. It depends of the temperature profile of the cooling extruder and of the specific heat of the blend PS / blowing agent.
Using these conditions, panels without any defects could be produced easily during a short period of time.
However, we could notice that the temperature of the melt increased progressively up to 128 °C and induced the formation of surface defects on the panels.
The cooling system was not efficient enough for this specific composition.
We took then the decision to increase the amount of gas up to 8.5 %.

3.2. NEW CONDITIONS

The pressure of the extruder has been increased to 230 bar and the gas flow rate has been set to 8.5 % (60 kg / h).
Even in these conditions, the temperature of the melt could not be reduced to 125 °C (optimal value).
It has been decided to slow the production rate in order to allow the system to cool down more easily. The PS flow rate has been reduced to 610 kg / h and the ratio of blowing agent has been kept constant (8.5 %).
The surface defect disappeared after equilibration of the line.
However, by slowing down the line, the temperature of the melt became too low (120 °C) reducing the efficiency of the foam expansion. Because of this, an increase of the density has been observed despite a higher amount of blowing agent.
In order to avoid a too big modification of the process, the six temperature zones of the cooling extruder have not been modified. The temperature of the melt has been monitored by changing the feeding speed of the extruder.
Once the equilibrium has been obtained (T close to 125 °C), panels without defects could be obtained. A measurement of the density gave a value close to 39 kg / m^3.

The gas flow rate has then been increased in order to reach a ratio of 9 %.
After equilibration, we observed a drop of temperature in the melt which had to be compensated by an increase of the line speed.
After stabilization of the line, the panels showed still some defects (holes).
This indicates that the solubility limit of this blend should be very close to 9 %.

3.3. PRODUCTION OF PANELS WITH DIFFERENT THICKNESSES

At the end of the trial, a production of panels with different thicknesses has been tried.
For this trial, the blowing agent ratio was 8.7 % and the PS flow rate was 610 kg / h.
The thickness of the panels has been changed from 40 mm up to 70 mm without any particular problems.

4. ANALYSIS OF THE GASES IN THE AIR

The MIRAN equipment has been used to measure the concentration of HFC-134a, HFC-152a and Ethanol in the air.

Two ranges of concentration have been detected.
One in the range of 500 ppm when the ratio of blowing agent was below 9 %.
One in the range of 1100 ppm when the ratio of blowing agent has been set to 9 %.

The average values are collected in table 3.

Blowing agent ratio	HFC-134a	HFC-152a	EtOH
8.5%	273 ppm	400 ppm	150 ppm
9 %	600 ppm	1200 ppm	300 ppm

These figures confirm the fact that the solubility limit of the blend is close to 9 %.

5. CONCLUSION

The trial performed with the blend HFC-134a / HFC-152a/ EtOH (30 / 70 / 5) gave good results. XPS panels could be produced without any surface defects but at a density close to 40 kg / m^3. It stays still higher than the current densities (35 kg / m^3) but it shows a clear improvement due to the higher amount of HFC-152a.
We also checked the influence of the temperature of the melt on the properties of the foam. The cooling capacity of the extruder seems to be limited especially when it is working at high flow rates.

6. ACTIONS

- Check the thermal conductivity of the panels at the initial time and after ageing (RU101 - PID/ASN)
- Check the closed cells content (RU101 - PID)
- Measure the concentration of gases in the XPS and check their relative diffusion coefficients (RU101 - PID/ASN)
- Organize a new meeting with BUBBLE&FOAM in order to comment the results and to propose a new trial (RU101 - PID).

CV of Dr. Pierre DOURNEL

Diploma : Ph. D. in Chemistry (specialty : organic and organometallic chemistry) from University Bordeaux I (in 1990)

Employed with SOLVAY S.A. since 1991 with the following responsibilities :

1991-1992 Research : Development of a process for the synthesis of polyphenylene sulfide

1992-1997 Research in the field of heterogeneous catalysis for ethylene polymerisation

1997-2004 Technical assistance for use of hydrofluorocarbons as foaming agent for polymer foam and as solvent

2004- Laboratory manager for H_2O_2 applications

Dr. Dournel is, in addition to the present application, inventor of the following patents/applications :

US 5380821 PROCESS FOR THE FABRICATION OF POLYSULPHUR ARYLENES

US 6303668 AZEOTROPIC OR PSEUDO-AZEOTROPIC COMPOSITIONS AND USE OF THESE COMPOSITIONS

US 6660709 COMPOSITIONS COMPRISING 1,1,1,3,3-PENTAFLUOROBUTANE AND USE OF SAID COMPOSITIONS

US 6743765 COMPOSITIONS COMPRISING 1,1,1,3,3-PENTAFLUOROBUTANE AND USE OF SAID COMPOSITIONS

US 6753304 COMPOSITIONS COMPRISING PERFLUOROBUTYL METHYL ETHER AND USE OF SAID COMPOSITIONS

WO02/00753 POLYURETHANE FOAMS, COMPOSITIONS USEFUL FOR THEIR FABICATION AND PROCESS FOR THE FABRICATION OF FOAMS

WO02/38718 SOLVENT COMPOSITIONS

WO2004/081092 HYDROFLUOROCARBON COMPOSITIONS